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Surface Acidity of Phosphotungstic Acid–Alumina Catalyst and Its Activity for Propylene–Ethylene Codimerization

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Phosphotungstic acid–alumina catalyst was more active than alumina for propylene–ethylene codimerization. To elucidate the difference in this catalytic activity, the structure of alumina, the amount of dehydration and the surface acidity in both catalysts were investigated by calcining the catalysts at temperatures from 300 to 800°C.

The excess amount of adsorbed water on alumina containing phosphotungstic acid (10 wt% as P_2W_{24} per Al_2O_3), over that on alumina which contributes to increasing the acid amount at the acid strength $H_0 \leq -5.6$, was thought to increase effectively the yield of pentenes.

INTRODUCTION

Many studies have been made on the reaction of olefins over $NiO-SiO_2$ (*1*), $NiO-SiO_2-Al_2O_3$ (*2–6*), $SiO_2-Al_2O_3$ (*7–10*) and Al_2O_3 (*11–13*) catalysts, dealing with the reaction mechanism, the surface structure of the catalysts, the nature of active sites, the surface acidity, etc.

The present authors have already reported on the activity and selectivity of phosphotungstic acid–alumina catalyst ($PW-Al_2O_3$) in propylene–ethylene codimerization (*14*). To obtain more detailed knowledge on the effects of phosphotungstic acid (PW) on the alumina catalyst, the nature of alumina in the presence of PW has been investigated by means of X-ray diffraction, differential scanning calorimetory (DSC), thermogravimetric analysis (TGA) and measurement of the surface acidity. On the basis of the results obtained for catalysts calcined in the temperature range from 300 to 1000°C, the relationship among the water content retained in the catalysts, the surface acidity and the catalytic activity for propylene–ethylene codimerization are herein discussed.

EXPERIMENTAL METHODS

Alumina used for this experiment was prepared as follows: Activated alumina [denoted as Al_2O_3(I)] supplied by Sumitomo Chemical Industries Co. Ltd., was crushed and sieved to 14–32 for the reaction and 200–300 mesh for the surface studies. γ-Alumina was prepared from aluminum isopropoxide (*15*) and seived to 14–32 mesh. α-Alumina was prepared by calcining the Al_2O_3(I) in air at 1000°C for 4 hr. Alumina (II) and (III) were prepared from alumina sols 100 and 300, respectively, by calcining at 500°C for 6 hr in air and sieving to 14–32 mesh after dried and moulded. These alumina sols 100 and 300, supplied by Nissan Chemical Industries, Ltd., contained 10% of alumina in aqueous solutions of chromic and formic acid, respectively.

In preparing $PW-Al_2O_3$ catalysts the aluminas were immersed into the aqueous solution of phosphotungstic acid, $2H_3PW_{12}O_{40}17H_2O$, supplied by Wako Pure Chemical Industries Co. Ltd., and calcined at temperatures from 300 to 1000°C after dried in air at 110°C for 12 hr.

The amount of phosphotungstic acid supported was 10 wt% as P_2W_{24} per Al_2O_3 (PW–Al_2O_3 catalyst of this composition showed the maximum activity for propylene–ethylene codimerization). Alumina (I) used for comparison with the PW–Al_2O_3(I) catalyst was immersed into water, dried and calcined under the conditions of the preparation of PW–Al_2O_3(I).

For the DSC and TGA measurments, 20.0 mg of PW–Al_2O_3(I), 17.5 mg of Al_2O_3(I) and 2.5 mg of PW were used without calcination after drying in air at 110°C for 12 hr. The amounts of Al_2O_3(I) and PW corresponded to the weights of each component in PW–Al_2O_3(I).

X-Ray powder diffraction diagrams were recorded with an X-ray diffractometer (Rigakudenki, D-2F Type) using Cu$K\alpha$ radiation and a Ni filter.

The TGA and DSC were measured by using a thermobalance and a differential scanning calorimeter (Rigakudenki, 8085 Type).

Surface acidity was measured by butylamine titration using the following indicators: dimethylaminoazobenzene ($H_0 = +3.3$), benzeneazodiphenylamine ($H_0 = +1.5$), dicinnamalacetone ($H_0 = -3.0$) and benzalacetophenone ($H_0 = -5.6$) (*16,17*).

The propylene–ethylene codimerization was carried out at 300°C in a continuous-flow system under atmospheric pressure. The reactor was a glass tube (14 mm i.d. and 30 cm length) and consisted of the catalyst bed and the (15 cm long) preheating section. In the catalyst bed, 6 ml of catalyst was charged and a thermocouple was inserted through the top of reactor. Prior to each reaction, the catalyst was treated *in situ* in a stream of dried N_2 for 1 hr at 300°C. The reaction conditions were as follows; the feed was equimolar mixture of propylene and ethylene (each purity 99%, supplied from Tomoe Shokai and Takachiho Chemical Industries Ltd. respectively) and the space velocity was 300 GHSV. The effluent materials were analyzed by gas chromatography using Simalite column (3 m) containing 25% diocthylaphthalate and He as carrier gas (30 ml/min) at 30°C.

Definitions

butenes yield

$$= \frac{\text{amount of produced butenes (g)}}{\text{amount of supplied ethylene (g)}} \times 100,$$

pentenes yield

$$= \frac{\text{amount of produced pentenes (g)}}{\text{amount of supplied ethylene (g)}} \times 100,$$

hexenes yield

$$= \frac{\text{amount of produced hexenes (g)}}{\text{amount of supplied propylene (g)}} \times 100,$$

molar distribution of products (mol %)

$$= \frac{\text{mol numbers of each product}}{\text{total mol numbers of products}} \times 100.$$

RESULTS AND DISCUSSION

Forms of Alumina in PW-Al_2O_3 Catalyst Calcined at Various Temperatures

Results of propylene–ethylene codimerization over various PW–Al_2O_3 catalysts, calcined at 550–600°C for 4 hr in air, are shown in Table 1. The catalyst PW–Al_2O_3(I) had a greater activity than PW–Al_2O_3(γ) or PW–Al_2O_3(α) and showed a reactivity similar to PW–Al_2O_3(II) or PW–Al_2O_3(III).

TABLE 1

PRODUCTS IN CODIMERIZATION OF PROPYLENE WITH ETHYLENE OVER PW-Al_2O_3 CATALYSTS COMPOSED OF DIFFERENT ALUMINAS

Catalyst (with alumina form)	Pentenes yield (wt%)	Distribution of products (mol%)		
		Butenes	Pentenes	Hexenes
PW–Al_2O_3(I)	12.0	28.2	32.8	39.0
PW–γ–Al_2O_3	2.5	16.9	56.1	27.0
PW–α–Al_2O_3	0	—	—	—
PW–Al_2O_3(II)	9.4	29.7	33.7	36.6
PW–Al_2O_3(III)	7.7	28.7	32.6	38.7

The structural changes of alumina in the PW–Al_2O_3(I) and Al_2O_3(I) calcined at various temperatures were observed by X-ray diffraction (Figs. 1 and 2). Our results were interpreted as follows, by comparing with the known X-ray diffraction diagrams of different aluminas (*18–22*). In the PW–Al_2O_3(I) catalyst, the structure of alumina was an amorphous form at calcination temperature below 300°C, an amorphous form partially with γ-type (amorphous $> \gamma$) at 500–600°C and γ-type whose crystallinity was very low, at 800°C. At 1000°C, however, the structure of the alumina was θ-type.

On the other hand, Al_2O_3(I) had an amorphous form similar to that of the PW–Al_2O_3(I) below 300°C but exhibited γ-type partially with amorphous form ($\gamma >$ amorphous) at about 500–600°C. Consequently, when calcined at about 500–600°C, the amorphous structure of Al_2O_3(I) containing PW is more abundant than that of Al_2O_3(I). At 800°C the alumina was a typical γ-type whose crystallinity was higher than in the case of PW–Al_2O_3(I). At 1000°C, the alumina exhibited α-type structure mixed with γ-type, different from the case of PW–Al_2O_3(I).

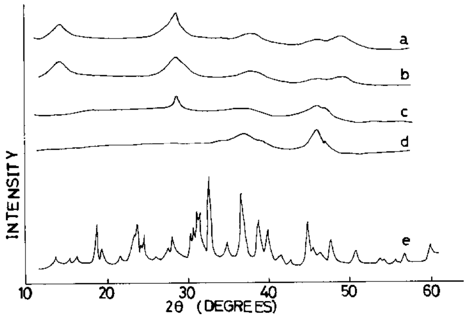

FIG. 1. X-Ray diffraction diagrams of PW–Al_2O_3(I) catalysts when dried at 100–110°C (a), and calcined at 300 (b), 500–600 (c), 800 (d), and 1000°C (e), for 4 hr in air.

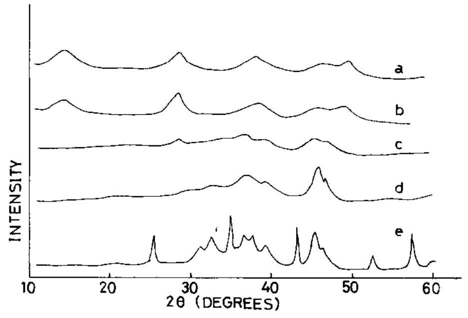

FIG. 2. X-Ray diffraction diagrams of Al_2O_3(I) when dried at 100–110°C (a), and calcined at 300 (b), 500–600 (c), 800 (d), and 1000°C (e), for 4 hr in air.

It may be concluded, therefore, that the alumina in PW–Al_2O_3(I) calcined at 600°C showing a maximum activity for the codimerization has an amorphous form partially with γ-type. Such structure persists up to higher calcination temperature than it does in the case of Al_2O_3(I) without PW.

Measurement of DSC of PW–Al_2O_3(I), Al_2O_3(I) and PW

The curves of DSC observed are shown in Fig. 3 and the amounts of the endothermic and exothermic heats are given in Table 2. The phosphotungstic acid is a heteropolytungstic acid and consists of groups of $PW_{12}O_{40}$ and H_2O (*23*). PW decomposes into phosphorus pentoxide and tungsten trioxide at 550–600°C (*24*); this was comfirmed from the exothermic peak in the range 520–610°C as shown in Fig. 3. In the case of PW–Al_2O_3(I), however, no

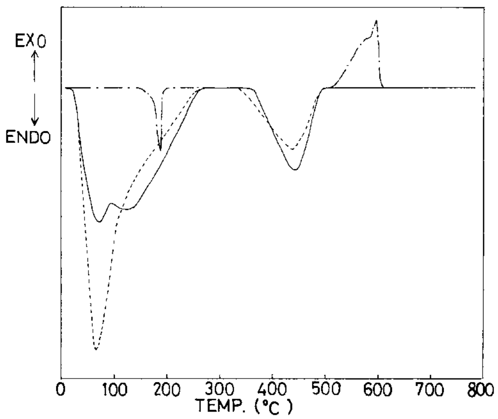

FIG. 3. DSC curves: (—) PW–Al_2O_3(I); (---) Al_2O_3(I); (—-) PW.

TABLE 2

EXOTHERMIC AND ENDOTHERMIC HEATS ESTIMATED BY DSC

Sample	Wt (mg)	Temp (°C)	Amount of heat (10^{-3} cal) Endothermic	Amount of heat (10^{-3} cal) Exothermic
$PW-Al_2O_3(I)$	20.0	265	1560.4	—
		365–500	474.2	—
		500	2034.6	—
$Al_2O_3(I)$	17.5	265	1843.2	—
		340–500	434.8	—
		500	2278.0	—
PW	2.5	150–200	54.6	—
		520–610	—	293.5

exothermic peak was observed in the range 500–800°C. Since $Al_2O_3(I)$ has no endothermic peak in the range 500–800°C, it is unlikely that the exothermic peak of PW and the endothermic peak of $Al_2O_3(I)$ compensate each other. Hence, the phosphotungstic acid in $PW-Al_2O_3(I)$ does not decompose below 800°C, although the heteropolytungstic acid is partially dehydrated.

Measurements of TGA of $PW-Al_2O_3(I)$ and $Al_2O_3(I)$

As shown in Table 3, two dehydration steps below and above 300°C were recognized in both $PW-Al_2O_3(I)$ and $Al_2O_3(I)$. The followings may be considered as reported by Peri and Hannan and De Boer *et al.* (*25*), that the water adsorbed in multilayer as undissociated molecules with hydrogen bonds desorbs below 300°C. The water remaining above 300°C, which is generally thought to be bound as hydroxyl groups, gradually desorbs up to 700°C.

Although the crystalline water of $PW(2H_3PW_{12}O_{40}17H_2O)$ would be almost dehydrated up to 600°C, the amount of dehydration of $PW-Al_2O_3(I)$ was smaller than that of $Al_2O_3(I)$ in the calcination up to 700°C. The amount of dehydration of 20.0 mg of $PW-Al_2O_3(I)$ up to 700°C was, also found to be less than that calculated by (a) and (b), where (a) is the amount of dehydration of 17.5 mg of $Al_2O_3(I)$ and (b), that of 2.5 mg of PW. This fact may be attributed to formation of a complex structure due to the coexistence of the partially dehydrated PW and the alumina which presumably adsorbs water dissociatively.

TABLE 3

AMOUNT OF DEHYDRATION FOR $PW-Al_2O_3(I)$, $Al_2O_3(I)$, PW AND OF THE CALCULATED DEHYDRATION AT VARIOUS CALCINATION TEMPERATURES

Calcination temp (°C)	% of dehydration (wt%) $Al_2O_3(I)$	PW	$PW-Al_2O_3(I)$	Calculated
200	13.1	2.0	8.2	11.7
300	15.2	3.2	10.5	13.7
400	17.3	3.2	12.5	15.6
500	20.0	3.6	15.5	18.0
600	21.0	4.0	16.1	18.9
700	21.5	4.0	16.5	19.4

The difference between the amount of retained water on $PW-Al_2O_3(I)$ and that on $Al_2O_3(I)$ may be the cause by which $PW-Al_2O_3(I)$ retains more abundantly the amorphous alumina mixed with γ-type than $Al_2O_3(I)$, in the calcination temperatures of 300 to 700°C.

Surface acidity of $PW-Al_2O_3(I)$ and Al_2O_3 (I)

Surface acidity of $PW-Al_2O_3(I)$ and $Al_2O_3(I)$ catalysts, calcined in air at temperatures from 300 to 1000°C for 4 hr, was measured as shown in Fig. 4a and b.

In each catalyst, the total acid amount at the acid strength, $H_0 \leq 3.3$ showed a maximum, when calcined at about 600°C and then fell to zero when the catalysts were calcined at 1000°C. Of the four ranges of acid strength, the acid amount varied most remarkably at the range $H_0 \leq -5.6$. It showed maxima at 600 and 500°C, respectively, in $PW-Al_2O_3(I)$ and $Al_2O_3(I)$. On the other hand, the acid amounts in the ranges other than $H_0 \leq -5.6$ have a minimum at about 600°C calcination.

Here, in order to elucidate the effect of

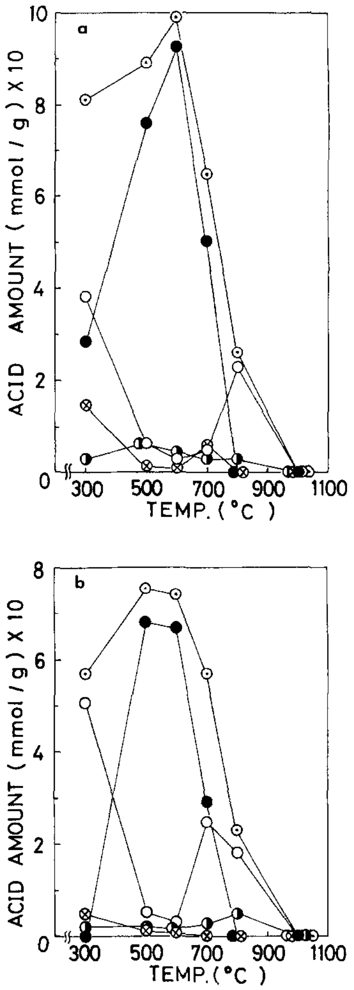

FIG. 4a and b. Acid amounts of PW–Al_2O_3(I) and Al_2O_3(I) against calcination temperatures. (a) PW–Al_2O_3(I), (b) Al_2O_3(I). (●) $H_0 \leqslant -5.6$, (○) $-5.6 < H_0 \leqslant -3.0$, (⊗) $-3.0 < H_0 \leqslant 1.5$, (◑) $1.5 < H_0 \leqslant 3.3$, (⊙) $H_0 \leqslant 3.3$.

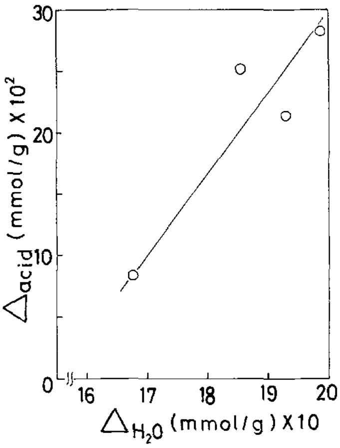

FIG. 5. Relation between Δ_{acid} and Δ_{H_2O} in the calcination at 300, 500, 600 and 700°C.

PW on Al_2O_3(I), let us compare the difference in the acid amounts at $H_0 \leqslant -5.6$ between PW–Al_2O_3(I) and Al_2O_3(I), Δ_{acid}, with the difference in the amounts of dehydrated water of PW–Al_2O_3(I) between calculated one from (a) + (b) and observed one, Δ_{H_2O}.

As shown in Fig. 5, an almost linear relationship is set up between Δ_{acid} and Δ_{H_2O}. Such linear relation was not recognized in the acid strength ranges other than $H_0 \leqslant -5.6$. It may be concluded accordingly that the excess amount of water retained in PW–Al_2O_3(I) over that in Al_2O_3(I), presumably behaves as Brönsted acid sites (*11,26*), and contributes to increase the acid amount at $H_0 \leqslant -5.6$.

Activity of PW–Al_2O_3(I) Catalyst for Propylene–Ethylene Codimerization

The activity for propylene–ethylene codimerization at 300°C over PW–Al_2O_3(I) and Al_2O_3(I), calcined at temperatures

TABLE 4

REACTION PRODUCTS OF PROPYLENE WITH ETHYLENE OVER PW–Al_2O_3(I) AND Al_2O_3(I) CALCINED AT VARIOUS TEMPERATURES

Calcination temp (°C)	Catalyst[a]	Yield (%)		
		Pentenes	Butenes	Hexenes
300	a	4.3	2.3	8.4
	b	Tr	—	—
500	a	9.9	4.7	12.5
	b	7.2	3.3	9.3
600	a	12.0	8.3	11.4
	b	6.0	6.1	8.2
700	a	6.0	1.9	9.1
	b	2.9	0.8	8.9
800	a	Tr	—	—
	b	0	—	—

[a] a: PW-Al_2O_3(I); b: Al_2O_3(I).

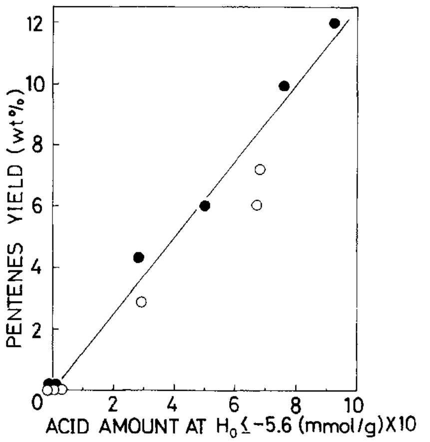

FIG. 6. Relation between pentenes yield and the acid amount at $H_0 \leq -5.6$, on PW–Al_2O_3(I) and Al_2O_3(I) calcined at various temperatures. (●) PW–Al_2O_3(I), (○) Al_2O_3(I).

from 300 to 1000°C for 4 hr in air, is given in Table 4. The pentenes yield was increased by the support of PW on Al_2O_3(I) and showed a maximum at 600°C. Furthermore, a linear relation was recognized between the pentenes yield and the acid amount at $H_0 \leq -5.6$, as shown in Fig. 6. On the other hand, the yield of butenes or hexenes produced by the dimerization of ethylene or propylene, respectively, has no linear relation with the acid amount in four acid strength ranges.

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